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(54) SILVER OXIDE-CARBON COMPOSITE MATERIAL AND ACTIVE MATERIAL FOR POSITIVE ELECTRODE OF SILVER OXIDE SECONDARY BATTERY AND PRODUCING METHOD OF SILVER OXIDE-CARBON COMPOSITE MATERIAL

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a silver oxide-carbon composite material, capable of raising charge and discharge efficiency and prolonging lifetime of a silver oxide secondary battery and to provide its producing method.

SOLUTION: Formation of particle of silver oxide (I) and coating on the surface of the particle with the carbon particle are accomplished by adding alkaline solution to water solution of silver salt, containing a powder with an average diameter for carbon particle of 900 Å or smaller. According to the producing method, since the particle growth of silver oxide (I) (Ag_2O) is obstructed by the carbon particle, silver oxide-carbon composite material of a small average diameter coated over whole surface with carbon particles is obtained readily.

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(54)【発明の名称】 酸化銀-炭素複合材料及び酸化銀2次電池用の正極活物質及び酸化銀-炭素複合材料の製造方法

(57)【要約】

【課題】 酸化銀2次電池の充放電効率を高くし、サイクル寿命の長くすることが可能な酸化銀-炭素複合材料及びその製造方法を提供する。

【解決手段】 平均粒径900Å以下の炭素粒子粉末を含有する銀塩水溶液中に塩基性溶液を添加することにより、酸化銀(I)粒子を形成すると共に該粒子の表面を前記炭素粒子で被覆させることを特徴とする酸化銀-炭素複合材料の製造方法を採用する。かかる製造方法によれば、酸化銀(I)(Ag₂O)粒子の粒成長が炭素粒子によって阻害されるので、平均粒径が小さく、かつ表面全体が炭素粒子により被覆された酸化銀-炭素複合材料を容易に得ることができる。

【特許請求の範囲】

【請求項1】 酸化銀(I)粒子が微細な炭素粒子により被覆されてなることを特徴とする酸化銀-炭素複合材料。

【請求項2】 酸化銀(I)粒子内に微細な炭素粒子が包含されるとともに、前記酸化銀(I)粒子が該炭素粒子により被覆されてなることを特徴とする酸化銀-炭素複合材料。

【請求項3】 前記酸化銀(I)粒子の平均一次粒子径が1.5μm以下であり、前記炭素粒子の平均粒径が50Å以上900Å以下であることを特徴とする請求項1または請求項2のいずれかに記載の酸化銀複合材料。

【請求項4】 2t/cm²の圧力で圧密化されたときの比抵抗が1000Ω·cm以下であることを特徴とする請求項1ないし請求項3のいずれかに記載の酸化銀-炭素複合材料。

【請求項5】 請求項1ないし請求項4のいずれかに記載の酸化銀-炭素複合材料からなることを特徴とする酸化銀2次電池用の正極活物質。

【請求項6】 請求項5に記載の酸化銀2次電池用の正極活物質を具備してなることを特徴とする酸化銀2次電池。

【請求項7】 平均粒径900Å以下の炭素粒子粉末を含有する銀塩水溶液中に塩基性溶液を添加して、酸化銀(I)粒子を析出させつつ、前記炭素粒子を前記酸化銀(I)粒子の表面に被覆させることを特徴とする酸化銀-炭素複合材料の製造方法。

【請求項8】 平均粒径900Å以下の炭素粒子粉末を含有する塩基性水溶液中に銀塩水溶液を添加して、酸化銀(I)粒子を析出させつつ、前記炭素粒子を前記酸化銀(I)粒子の表面に被覆させることを特徴とする酸化銀-炭素複合材料の製造方法。

【請求項9】 酸化銀(I)粒子を析出させる際に、酸化銀(I)粒子内に前記炭素粒子を包含させることを特徴とする請求項7または請求項8に記載の酸化銀-炭素複合材料の製造方法。

【請求項10】 前記銀塩水溶液中に含まれる銀と前記炭素粒子粉末の重量比をA:Bとしたとき(Aは銀塩溶液中の銀の重量であり、Bは炭素粒子粉末の重量である)、前記A:Bが80:20~98:2の範囲であることを特徴とする請求項7または請求項8に記載の酸化銀-炭素複合材料の製造方法。

【請求項11】 炭素粒子により表面が被覆された前記の酸化銀(I)粒子を、90°C以下で乾燥することを特徴とする請求項7ないし請求項10のいずれかに記載の酸化銀-炭素複合材料の製造方法。

【請求項12】 炭素粒子により表面が被覆された前記の酸化銀(I)粒子を、真空乾燥することを特徴とする請求項7ないし請求項10のいずれかに記載の酸化銀-炭素複合材料の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、酸化銀-炭素複合材料、酸化銀2次電池用の正極活物質及び酸化銀-炭素複合材料の製造方法に関するものである。

【0002】

【従来の技術】酸化銀を正極活物質とする電池には、酸化銀1次電池と酸化銀2次電池とがある。このうち、酸化銀1次電池は正極合剤として、正極活物質である酸化銀(I)(Ag₂O)の粉末と、導電助剤である炭素粒子粉末または銀ニッケライト粉末を混合したものを用いている。酸化銀(I)(Ag₂O)は導電性が低いものであるが、放電反応の進行により還元されて導電性の金属銀(Ag)になり、正極合剤の導電性が放電の進行と共に向上する。また、炭素粒子粉末や銀ニッケライト粉末は、放電初期の導電材として作用する。これは、放電初期においては正極合剤の酸化銀(I)(Ag₂O)の含有率が高いために正極合剤の導電性が低くなるため、上記の導電助剤を添加して正極合剤の導電性を高める必要があるからである。

【0003】一方、酸化銀2次電池は、酸化銀1次電池と同様に正極合剤に正極活物質である酸化銀(I)(Ag₂O)粉末と導電助剤である炭素粒子粉末を含み、放電時には導電性の低い酸化銀(I)(Ag₂O)が導電性の高い金属銀(Ag)まで還元され、充電時においては金属銀(Ag)が酸化銀(I)(Ag₂O)まで酸化される。この金属銀と酸化銀(I)の間の可逆的な酸化還元反応は、金属銀粒子または酸化銀(I)粒子の表面から各粒子の内部に向けて反応が進行する。従って、特に充放電深度が深い場合、金属銀粒子の表面に導電性の低い酸化銀(I)が厚く形成し、電子の授受が困難になって十分に充電できなくなるおそれがある。

【0004】そこで、酸化銀(I)粒子の平均粒径を0.1~0.3μmと小さくすることによって酸化銀(I)の析出に伴う導電性低下の影響をできるだけ小さくし、これにより充電を円滑に進めさせて充放電特性を改善した酸化銀2次電池に関する発明が開示されている(特開昭57-111955号)。

【0005】

【0005】40 【発明が解決しようとする課題】しかし、従来の酸化銀2次電池では、正極合剤中に含まれる炭素粒子粉末が編析する場合があり、正極合剤全体の導電性を高めることができないという問題があった。

【0006】また、前記の特開昭57-111955号においては、充放電深度50%での充放電試験でも最高で7サイクル程度しか充放電することができておらず、サイクル寿命が短く実用的な電池を得るには至っていないかった。これは、充電末期に絶縁物である酸化銀(I)が析出するため、正極合剤の導電性が低下するためであつた。

【0007】本発明は上記事情に鑑みてなされたものであって、正極合剤の導電性を向上させ、酸化銀2次電池の充放電効率を高くし、かつサイクル寿命の長くすることとが可能な酸化銀-炭素複合材料及びその製造方法を提供することを目的とする。

【0008】

【課題を解決するための手段】上記の目的を達成するために、本発明は以下の構成を採用した。本発明の酸化銀-炭素複合材料は、酸化銀(I)粒子が微細な炭素粒子により被覆されてなることを特徴とする。また本発明の酸化銀-炭素複合材料は、酸化銀(I)粒子内に微細な炭素粒子が含まれるとともに、前記酸化銀(I)粒子が該炭素粒子により被覆されてなることを特徴とする。

【0009】前記酸化銀(I)粒子の平均一次粒子径は1.5μm以下であることが好ましく、前記炭素粒子の平均粒径は50Å以上900Å以下であることが好ましい。また、前記酸化銀(I)粒子の平均一次粒子径は0.1μm以上1.5μm以下であることがより好ましく、0.2μm以上1.0μm以下であることがさらに好ましい。また前記炭素粒子の平均粒径は100Å以上50Å以下であることがより好ましい。

【0010】かかる酸化銀-炭素複合材料は、酸化銀(I)粒子の表面に満遍なく炭素粒子が被覆形成されるか、あるいは酸化銀(I)粒子の内部に炭素粒子が含まれるとともに酸化銀(I)粒子の表面に炭素粒子が被覆形成されてなり、この酸化銀-炭素複合材料の粉末が圧密されると炭素粒子によって導電性ネットワークが形成されるので、この酸化銀-炭素複合材料を酸化銀2次電池用の正極活物質として用いた場合には、充電の進行に伴って酸化銀が生成したとしても正極活物質の比抵抗が高くなることがなく、酸化銀2次電池の充放電効率を高くすることができる。また、酸化銀(I)粒子の平均一次粒子径が上記の範囲であれば、充放電反応を効率よく進めることができ、酸化銀2次電池の充放電効率を高くすることができる。

【0011】また本発明の酸化銀-炭素複合材料は、2t/cm²の圧力で圧密化したときの比抵抗が1000Ω·cm以下であるものが好ましく、300Ω·cm以下であるものがより好ましい。

【0012】かかる酸化銀-炭素複合材料によれば、圧密時の比抵抗が1000Ω·cm以下であるので、この酸化銀-炭素複合材料を酸化銀2次電池用の正極活物質として用いた場合には、充電末期における酸化銀2次電池の正極合剤の比抵抗を低くすることができ、充電効率を高くできる。

【0013】本発明の酸化銀2次電池用の正極活物質は、上記の酸化銀-炭素複合材料よりなるものである。そして本発明の酸化銀2次電池は、上記の酸化銀2次電池用の正極活物質を具備してなるものである。かかる酸化銀2次電池は、上記の正極活物質を具備しているの

で、正極合剤の導電率を高くでき、充放電効率を高くできると共にサイクル寿命を大幅に伸ばすことができる。

【0014】本発明の酸化銀-炭素複合材料の製造方法は、平均粒径900Å以下の炭素粒子粉末を含有する銀塩水溶液中に塩基性溶液を添加して、酸化銀(I)粒子を析出させつつ、前記炭素粒子を前記酸化銀(I)粒子の表面に被覆させることを特徴とする。また、平均粒径900Å以下の炭素粒子粉末を含有する塩基性水溶液中に銀塩溶液を添加して、酸化銀(I)粒子を析出させつつ、前記炭素粒子を前記酸化銀(I)粒子の表面に被覆させるものでもよい。前記炭素粒子が銀塩水溶液中に懸濁していると、酸化銀(I)粒子を析出させる際に酸化銀(I)粒子内に前記炭素粒子を包含させやすくなる。

【0015】上記の炭素粒子としては、カーボンブラック粒子、メソフェーズピッチ粒子、ピッチ粒子、グラファイト粒子等の、平均粒径が900Å以下、好ましくは50Å以上900Å以下、より好ましくは100Å以上500Å以下のものが良い。また上記の銀塩水溶液としては、硝酸銀等の水溶液を例示できる。更に上記の塩基性溶液としては、水酸化カリウム、水酸化ナトリウム等の塩基性水溶液を例示できる。

【0016】例えば硝酸銀水溶液等の銀塩水溶液に水酸化カリウム水溶液等の塩基性溶液を添加すると、酸化銀(I)(Ag₂O)が析出する。銀塩溶液中に微細な炭素粒子が懸濁状態で添加されていると、酸化銀(I)(Ag₂O)粒子の粒成長が炭素粒子によって阻害され、酸化銀(I)粒子の平均粒径が小さくなる。更に懸濁している炭素粒子が酸化銀(I)粒子の表面に沈着し、酸化銀(I)粒子が炭素粒子により被覆される。また、酸化銀(I)粒子が析出する際に炭素粒子が酸化銀(I)粒子内に取り込まれる場合もある。従って、かかる酸化銀2次電池用の酸化銀の製造方法によれば、平均粒径が小さく、表面全体が炭素粒子により被覆された酸化銀(I)粒子を容易に得ることができる。

【0017】また、前記銀塩水溶液中に含まれる銀と前記炭素粒子粉末との重量比をA:Bとしたとき(Aは銀塩溶液中の銀の重量であり、Bは炭素粒子粉末の重量である)、前記A:Bが80:20~98:2の範囲であることが好ましい。また、上記A:Bは、88:12~96:4であることがより好ましい。炭素粒子粉末と銀との重量比が上記範囲内にあれば、酸化銀(I)粒子表面に炭素粒子を満遍なく被覆させることができる。

【0018】更に、炭素粒子により表面が被覆された前記の酸化銀(I)粒子を、90°C以下、好ましくは70°C以下で乾燥することが好ましい。このときの乾燥雰囲気は、大気中あるいは不活性ガス雰囲気中で行うことが好ましい。また、炭素粒子により表面が被覆された前記の酸化銀(I)粒子を真空乾燥しても良い。真空乾燥する際の乾燥温度は、70°C以下とすることが好ましく、冷凍真空乾燥してもよい。

【0019】炭素粒子により表面が被覆された前記の酸化銀(I)粒子を、上記の条件の範囲内で乾燥すれば、乾燥中に炭素粒子と酸化銀(I)粒子とが燃焼反応することがない。

【0020】

【発明の実施の形態】以下、本発明の実施の形態を図面を参照して説明する。本発明酸化銀-炭素複合材料は、酸化銀(I)(Ag₂O)粒子が微細な炭素粒子により被覆されてなるものである。また、本発明の酸化銀-炭素複合材料は、酸化銀(I)粒子内に微細な炭素粒子が含まれるとともに、前記酸化銀(I)粒子が炭素粒子により被覆されてなるものであってもよい。

【0021】本発明の酸化銀-炭素複合材料は、酸化銀1次電池または酸化銀2次電池の正極活物質として用いられるもので、特に酸化銀2次電池に用いられることが好ましい。この酸化銀-炭素複合材料が酸化銀1次電池に用いられる場合は、放電の際に酸化銀(I)(Ag₂O)が導電性の金属銀(Ag)まで還元される。また、酸化銀-炭素複合材料が酸化銀2次電池に用いられる場合は、放電時に酸化銀(I)(Ag₂O)が導電性の金属銀(Ag)まで還元され、充電時には金属銀(Ag)が酸化銀(I)(Ag₂O)まで酸化される。酸化銀2次電池における金属銀と酸化銀(I)の間の可逆的な酸化還元反応は、金属銀粒子または酸化銀(I)粒子の表面から各粒子の内部に向けて反応が進行する。従って、特に充放電深度が深い場合、金属銀粒子の表面に絶縁物である酸化銀(I)が厚く形成し、電子の授受が困難になって十分に充電できなくなるおそれがある。

【0022】そこで、本発明では、酸化銀(I)粒子の表面に溝遍なく炭素粒子を被覆形成してなる酸化銀-炭素複合材料を構成した。この酸化銀-炭素複合材料の粉末が圧密されて酸化銀2次電池の正極合剤が形成されると、炭素粒子によって導電性ネットワークが形成される。従って、充電の進行に伴って絶縁物である酸化銀が生成したとしても、炭素粒子の導電性ネットワークにより酸化銀-炭素複合材料自体の比抵抗が高くなることがなく、充放電効率を高くできる。また、酸化銀(I)粒子内に炭素粒子が含まれると、酸化銀(I)粒子自体の導電性を向上させることができ、酸化銀-炭素複合材料自体の比抵抗が高くなることがなく、酸化銀2次電池の充放電効率を高くできる。

【0023】また、炭素粒子は酸化銀(I)粒子の表面を溝遍なく均一に被覆することが好ましい。炭素粒子が酸化銀(I)粒子を溝遍なく被覆しないと、炭素粒子が偏析することになり、均一な導電性ネットワークを形成できなくなってしまって充放電効率が低下してしまうので好ましくない。

【0024】本発明の酸化銀-炭素複合材料は、酸化銀(I)粒子の平均一次粒子径が1.5μm以下、より好ましくは0.1μm以上1.5μm以下、更に好ましくは

0.2μm以上1.0μm以下のものであると良い。酸化銀(I)粒子の平均一次粒径が1.5μmを越えると、充電時に酸化銀(I)が金属銀を厚く覆うことになり、それ以上金属銀を酸化することができなくなってしまって充電反応が阻害され、充放電効率が低下してしまうので好ましくない。また平均一次粒径が0.1μm未満であると、酸化銀(I)の一部が酸化銀(I)粒子を覆う炭素粒子により放電生成物である金属銀まで還元されてしまい、酸化銀2次電池の自己放電率が高くなってしまうので好ましくない。酸化銀(I)粒子の平均一次粒子径が上記の範囲内であれば、充放電反応を効率よく進めることができ、充放電効率を高くすることができる。

【0025】また、酸化銀(I)粒子を覆う炭素粒子の平均粒径は50Å以上900Å以下であることが好ましく、100Å以上500Å以下であることがより好ましい。炭素粒子の平均粒径が50Å未満であると、炭素粒子の活性が非常に高くなり、酸化銀(I)を金属銀に還元してしまうおそれがあり、酸化銀2次電池の自己放電率が高くなってしまうので好ましくない。また炭素粒子の平均粒径が900Åを越えると、炭素粒子が酸化銀(I)粒子を溝遍なく被覆できなくなり、導電性ネットワークを形成できなくなるので好ましくない。

【0026】また本発明の酸化銀-炭素複合材料は、2t/cm²の圧力で圧密化したときの比抵抗が1000Ω·cm以下であることが好ましく、300Ω·cm以下であることがより好ましい。比抵抗が1000Ω·cmを越えると、酸化銀2次電池の正極合剤の導電性が低下することになり、充放電効率が低下するので好ましくない。比抵抗は、酸化銀(I)粒子を覆う炭素粒子の被覆状態に大きく左右される。即ち炭素粒子が酸化銀(I)粒子の表面で偏在すると比抵抗が高くなる。このことからも炭素粒子は酸化銀(I)粒子を溝遍なく均一に被覆することが好ましい。

【0027】上記の酸化銀-炭素複合材料は、酸化銀2次電池の正極活物質として好適に用いることができる。ここで酸化銀2次電池としては、いわゆるボタン型の酸化銀2次電池を例示することができる。この酸化銀2次電池は、本発明の酸化銀-炭素複合材料粉末の単独あるいは酸化銀-炭素複合材料粉末に黒鉛等の導電助剤を添加したものをペレット状に成形した正極合剤と、負極ゲル亜鉛と、セパレータと、電解液と、これらを収納する電池容器とによって構成される。

【0028】負極ゲル亜鉛は、例えれば亜鉛粉に水銀を添加してアマルガム化した汞化亜鉛粉と、カルボキシメチルセルロース等のゲル化剤と、電解液とを混合してなるものである。また電解液は、水酸化ナトリウム、水酸化カリウムのうちのいずれか一方の水溶液あるいはこれらの混合溶液に、酸化亜鉛を溶解させたものを用いることができる。更にセパレータは、銀イオンの拡散を防ぐためにセロハンを主体として構成されるもので、セロハン

に例えばグラフト化処理されたポリエチレンを積層して構成される。

【0029】次に本発明の酸化銀-炭素複合材料の製造方法について説明する。本発明の酸化銀-炭素複合材料の製造方法は、平均粒径900Å以下の炭素粒子粉末を含有する銀塩水溶液中に塩基性溶液を添加することにより、酸化銀(I)粒子を析出させつつ、前記炭素粒子を前記酸化銀(I)粒子の表面に被覆させるというものである。炭素粒子は銀塩水溶液中で懸濁していることが好ましい。また、平均粒径900Å以下の炭素粒子粉末を含有する塩基性水溶液中に銀塩性溶液を添加してもよい。また、酸化銀(I)粒子を析出させる際に、酸化銀(I)粒子内に前記炭素粒子を包含させてもよい。

【0030】例えば硝酸銀水溶液等の銀塩水溶液に、水酸化カリウム水溶液等の塩基性溶液を添加すると、酸化銀(I)(Ag₂O)が析出する。ここで、銀塩溶液中に微細な炭素粒子が懸濁状態で添加されていると、酸化銀(I)(Ag₂O)粒子の粒成長が炭素粒子によって阻害され、酸化銀(I)粒子の平均粒径が小さくなる。更に懸濁している炭素粒子が酸化銀(I)粒子の表面に沈着し、酸化銀(I)粒子が炭素粒子により被覆される。また、酸化銀(I)粒子が析出する際に炭素粒子が酸化銀(I)粒子内に取り込まれる場合もある。従って、かかる酸化銀-炭素複合材料の製造方法によれば、平均粒径が小さく、かつ表面全体が炭素粒子により被覆された酸化銀(I)粒子を容易に得ることができる。

【0031】上記の炭素粒子としては、カーボンブラック粒子、メソフェーズピッチ粒子、ピッチ粒子、グラファイト粒子等の、平均粒径が900Å以下、好ましくは50Å以上900Å以下、より好ましくは100Å以上500Å以下のものが良い。炭素粒子の平均粒径が50Å未満だと、炭素粒子の活性が非常に高くなつて、後述する酸化銀(I)の乾燥時に炭素粒子が着火するおそれがあり、また酸化銀(I)を金属銀に還元してしまうおそれがあるので好ましくない。また炭素粒子の平均粒径が900Åを越えると、酸化銀(I)を生成させる際に酸化銀(I)の粒成長を効果的に阻害することができなくなつて酸化銀(I)粒子が肥大化してしまうおそれがあり、また炭素粒子によって酸化銀(I)粒子を満遍なく被覆することができなくなつて導電性ネットワークを形成できなくなるおそれがあるので好ましくない。

【0032】また上記の銀塩水溶液としては、硝酸銀等の銀塩水溶液を例示できる。更に上記の塩基性溶液としては、水酸化カリウム、水酸化ナトリウム等の塩基性水溶液を例示できる。

【0033】また、銀塩水溶液中に含まれる銀と前記炭素粒子粉末との重量比をA:Bとしたとき(Aは銀塩溶液中の銀の重量であり、Bは炭素粒子粉末の重量である)、前記A:Bが80:20~98:2の範囲であることが好ましく、88:12~96:4であることがよ

り好ましい。重量比A:B=80:20の場合よりも銀の重量比(A)が小さくなると、得られる酸化銀-炭素複合材料の成形性が低下するため、酸化銀-炭素複合材料の粉末を圧密化して正極合剤を成形した際に正極合剤が割れやすくなるので好ましくない。また、A:B=98:2の場合よりも銀の重量比(A)が大きくなると、炭素粒子量が不足して酸化銀(I)粒子に対して炭素粒子が偏在してしまい、炭素粒子を酸化銀(I)粒子表面に満遍なく均一に被覆させることができなくなるので好ましくない。炭素粒子粉末と銀との重量比が上記範囲内にあれば、酸化銀(I)粒子表面に炭素粒子を満遍なく被覆させることができ、また成形性に優れた酸化銀-炭素複合材料が得られる。

【0034】具体的には、銀塩水溶液に含まれる銀の濃度が40g/L以上700g/L以下の範囲であることが好ましく、200g/L以上500g/L以下の範囲であることがより好ましい。また、銀塩水溶液または塩基性水溶液に含まれる炭素粒子粉末の濃度が3g/L以上60g/L以下の範囲であることが好ましく、10g/L以上30g/L以下の範囲であることがより好ましい。

【0035】炭素粒子により被覆された酸化銀(I)粒子は、90°C以下、好ましくは70°C以下で乾燥することが好ましい。このときの乾燥雰囲気は、大気中あるいは不活性ガス雰囲気中で行なうことが好ましい。乾燥温度が90°Cを越えると、炭素粒子が着火するおそれがあり、また酸化銀(I)を金属銀に還元してしまうおそれがあるので好ましくない。

【0036】また、上記の加熱乾燥に代えて、炭素粒子により被覆された酸化銀(I)粒子を真空乾燥することがより好ましい。真空乾燥する際の乾燥温度は、70°C以下のとすることが好ましく、冷凍乾燥しても良い。炭素粒子は加熱されると反応して酸化銀(I)を還元しやすく、この反応を防ぐためには室温での真空乾燥、あるいは10°C以下の低温真空乾燥、更には、-5°C以下の冷凍真空乾燥を行うことが有効である。

【0037】炭素粒子により被覆された酸化銀(I)粒子の乾燥を上記の条件の範囲内で行なえば、炭素粒子と酸化銀(I)粒子とが反応することなく、酸化銀-炭素複合材料を乾燥することができる。

【0038】上記の酸化銀-炭素複合材料は、酸化銀(I)粒子の表面に満遍なく炭素粒子が被覆形成されてなり、この粉末が圧密されると炭素粒子によって導電性ネットワークが形成されるので、充電の進行に伴つて酸化銀が生成したとしても酸化銀-炭素複合材料の比抵抗が高くなることがなく、充放電効率を高くすることができる。

【0039】また、上記の酸化銀-炭素複合材料の製造方法によれば、酸化銀(I)(Ag₂O)粒子の粒成長が炭素粒子によって阻害され、更に懸濁している炭素粒子

が酸化銀(I)粒子の表面に沈着するので、平均粒径が小さく、かつ表面全体が炭素粒子により被覆された酸化銀(I)粒子からなる酸化銀-炭素複合材料を容易に得ることができる。

【0040】

【実施例】(実施例1～5の酸化銀-炭素複合材料の製造)銀濃度が400g/Lである硝酸銀水溶液に、平均粒径50～900Åのカーボンブラックを投入して懸濁状態とした。この硝酸銀溶液を攪拌しつつ、5規定の水酸化ナトリウム水溶液を、硝酸銀水溶液がpH13になるまで添加して酸化銀(I)を析出させた。なお、硝酸銀水溶液に水酸化ナトリウム水溶液を添加する際には、液温が25℃を維持するように温度調整を行った。次にこの酸化銀(I)に対してデカンテーションと蒸留水による攪拌洗浄を7回づつ繰り返した後、加熱乾燥あるいは真空乾燥を行った。このようにして実施例1～5の酸化銀-炭素複合材料の製造した。表1には、各酸化銀-炭素複合材料とカーボンブラックの平均粒径の対応を示す。また、硝酸銀水溶液中の銀とカーボンブラックの重量比を表1に併せて示す。更に乾燥条件を表1に併せて示す。

【0041】(比較例1～4の酸化銀-炭素複合材料の製造)銀濃度が40g/Lの硝酸銀水溶液を攪拌しつつ、0.5規定の水酸化ナトリウム水溶液を、硝酸銀水溶液がpH12になるまで添加して酸化銀(I)を析出させた。なお、硝酸銀水溶液に水酸化ナトリウム水溶液を添加する際には、液温が8℃を維持するように温度調整を行った。次にこの酸化銀(I)に対してデカンテーションと蒸留水による攪拌洗浄を7回繰り返した後、160℃で加熱乾燥した後、カーボンブラックを乾式混合した。このようにして比較例1の酸化銀を製造した。製造条件を表1に示す。更に、銀とカーボンブラックの重量比、カーボンブラックの平均粒径を変えたこと以外は実施例1～5と同様にして、比較例2～4の酸化銀-炭素複合材料を製造した。製造条件を表1に示す。

【0042】実施例1～5及び比較例1の酸化銀を走査型電子顕微鏡(SEM)により観察した。このとき撮影した実施例1及び比較例1のSEM写真を図1及び図2に示す。図1から明らかなように、実施例1の酸化銀-炭素複合材料の表面は、粒径約200Åの微細なカーボンブラック粒子により満遍なく被覆されていることが分かる。またカーボンブラック粒子の下は酸化銀(I)であると推定され、その平均1次粒子径は約1μmであることが分かる。また、実施例2～5の酸化銀-炭素複合材料を構成する酸化銀(I)の平均1次粒子径は表2に示すとおりであり、いずれも1.5μm以下であることが分かる。一方、比較例1の酸化銀の表面には、粒状の粒子が何ら見られず、またこの酸化銀の平均1次粒子径は表2より0.3μmであった。

【0043】次に、実施例1～5及び比較例1～4の酸

化銀-炭素複合材料の粉末1gをそれぞれ成形金型に入れ、2t/cm²の圧力で圧密化することにより、3m²×2.7mm×30mmの大きさの直方体状の圧密体を得た。なお、比較例1においては、比較例1の酸化銀に5重量%の平均粒径500Åのカーボンブラックを添加して圧密化した。そして各圧密体に比抵抗測定用の電極を取り付け、4端子法により比抵抗を測定した。結果を表2に示す。表2から明らかなように、実施例1～5の酸化銀-炭素複合材料は、いずれも比抵抗が1000Ω·cm以下であり、比較例1～3の酸化銀の比抵抗よりも小さいことが分かる。

【0044】比較例1の酸化銀にカーボンブラックが添加されているのも係わらず、比抵抗が実施例1～5の酸化銀-炭素複合材料より高くなつたのは、添加したカーボンブラックが均一に分散されず圧密体中に偏在したため、均一な導電性ネットワークが形成されなかつたためと推定される。また、比較例2の酸化銀は、製造時の銀とカーボンブラック(CB)の重量比が銀:CB=99:1であつて、カーボンブラックの重量比が小さかつたため、酸化銀粒子の表面をカーボンブラックで満遍なく被覆することができず、比抵抗が高くなつたものと考えられる。

【0045】次に、実施例1～5及び比較例1～4の酸化銀-炭素複合材料の粉末を圧密化して直径11mm、厚さ2mmの円板状の正極合剂とした。なお、比較例1では酸化銀の他に5重量%の平均粒径500Åのカーボンブラックを添加した。また、鉛を0.5重量%含む汞化亜鉛粉に、カルボキシメチルセルロースと水酸化ナトリウム水溶液を添加して負極ゲル亜鉛とした。これら正極合剂と負極ゲル亜鉛を電池容器に収納すると共に正極合剂と負極ゲル亜鉛をセロハン製のセパレータで隔離し、更に30重量%の水酸化ナトリウムに少量の酸化亜鉛を含む電解液を添加することにより、直径11.6mm、高さ4.2mmのボタン型の酸化銀2次電池を製造した。

【0046】得られた電池を、充電電流3mA、充電時間40時間、放電電流3mA、放電終止電圧1.0Vの条件で充放電を行つた。初回放電容量を100%としたときの、5、10、20回目の放電容量比を表2に示す。表2から明らかなように、実施例1～5の酸化銀2次電池の20回目の放電容量が1回目の放電容量の70%以上であるのに対して、比較例1の酸化銀2次電池の10回目の放電容量が1回目の放電容量の2.9%程度となっている。従つて実施例1～5の酸化銀-炭素複合材料によれば、比較例1の酸化銀よりも、充放電効率が高く、サイクル寿命が長い酸化銀2次電池を構成できることが分かる。また、比較例2及び比較例3の酸化銀電池

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は、酸化銀-炭素複合材料の比抵抗がいずれも高いため、充放電を円滑に行うことができず、放電容量が低下したものと考えられる。更に比較例4の酸化銀電池では、酸化銀-炭素複合材料を製造した際の乾燥温度が90°Cと高かったため、酸化銀の一部が還元されて銀が析*

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*出し、これにより放電容量が低下したものと考えられる。

【0047】

【表1】

	銀とカーボンブラック粒子(CB)の重量比	カーボンブラック粒子の平均粒径(Å)	乾燥条件
実施例1	銀:CB=90:10	200	真空、10°C
実施例2	銀:CB=88:12	400	真空、-7°C(冷凍)
実施例3	銀:CB=96:4	100	大気、60°C
実施例4	銀:CB=97:3	60	大気、25°C
実施例5	銀:CB=82:18	800	真空、60°C
比較例1	銀:CB=96:4	400	-
比較例2	銀:CB=99:1	100	真空、60°C
比較例3	銀:CB=90:10	1500	真空、60°C
比較例4	銀:CB=90:10	100	真空、90°C

【0048】

※※【表2】

	カーボンブラック粒子の平均粒径(Å)	酸化銀(I)の平均1次粒子径(μm)	圧密体の比抵抗(Ω·cm)	5回目放電容量比(%)	10回目放電容量比(%)	20回目放電容量比(%)
実施例1	200	0.5	120	81	79	75
実施例2	400	1.0	230	79	75	74
実施例3	100	0.4	170	80	78	74
実施例4	60	0.2	610	78	74	71
実施例5	800	1.4	850	77	73	70
比較例1	400	0.3	11500	38	29	15
比較例2	100	0.9	5700	51	48	44
比較例3	1500	1.6	6500	57	51	46
比較例4	100	0.4	15	65	60	49

【0049】

【発明の効果】以上、詳細に説明したように、本発明の酸化銀-炭素複合材料は、酸化銀(I)粒子の表面に満遍なく炭素粒子が被覆形成されてなり、この酸化銀-炭素複合材料の粉末が圧密されると炭素粒子によって導電性ネットワークが形成されるので、充電の進行に伴って酸化銀が生成したとしても酸化銀-炭素複合材料の比抵抗が高くなることがなく、酸化銀2次電池の充放電効率を高くすることができる。また、酸化銀(I)粒子の平均一次粒子径が1.5μm以下であるので、充放電反応を効率よく進めることができ、酸化銀2次電池の充放電効率を高くすることができる。また、酸化銀(I)粒子を覆う炭素粒子の平均粒径が900Å以下であるので、炭素粒子によって酸化銀(I)粒子を満遍なく被覆することができる。

★【0050】また、本発明の酸化銀-炭素複合材料によれば、圧密時の比抵抗が1000Ω·cm以下であるので、充電末期における酸化銀2次電池の正極合剤の比抵抗を低くすることができ、酸化銀2次電池の充電効率を高くできる。尚、本発明の酸化銀-炭素複合材料を一旦顆粒化してから正極合剤を製造することもできる。

【0051】また本発明の酸化銀2次電池は、酸化銀(I)粒子の表面に満遍なく炭素粒子が被覆形成されてなる正極活性物質を具備してなるので、充放電効率を高くできると共にサイクル寿命を大幅に伸ばすことができる。

【0.0.5.2】本発明の酸化銀-炭素複合材料の製造方法は、平均粒径900Å以下の炭素粒子粉末を含有する銀塩水溶液中に塩基性溶液を添加することにより、酸化銀(I)粒子を形成すると共に該粒子の表面を前記炭素粒子で被覆させるので、酸化銀(I)(Ag₂O)粒子の粒成

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長が炭素粒子によって阻害され、更に懸濁している炭素粒子が酸化銀(I)粒子の表面に沈着し、平均粒径が小さく、かつ表面全体が炭素粒子により被覆された酸化銀(I)粒子を容易に得ることができる。

【0053】また、前記銀塩水溶液中に含まれる銀と前記炭素粒子粉末との重量比をA:Bとしたとき(Aは銀塩溶液中の銀の重量であり、Bは炭素粒子粉末の重量である)、前記A:Bが80:20~98:2の範囲であるので、酸化銀(I)粒子表面に炭素粒子を満遍なく被覆

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させることができる。

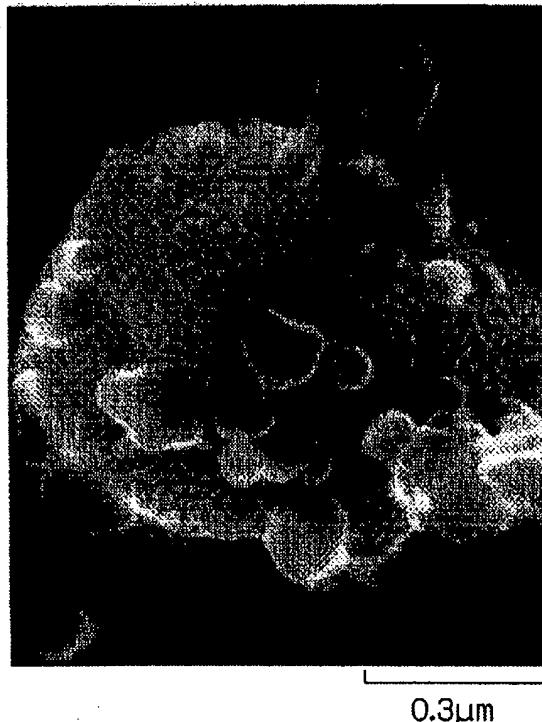
【0054】更に、炭素粒子により被覆された酸化銀(I)粒子を、90°C以下で乾燥するとか、または真空乾燥すれば、炭素粒子の着火あるいは炭素粒子による酸化銀(I)の還元を防止することができる。

【図面の簡単な説明】

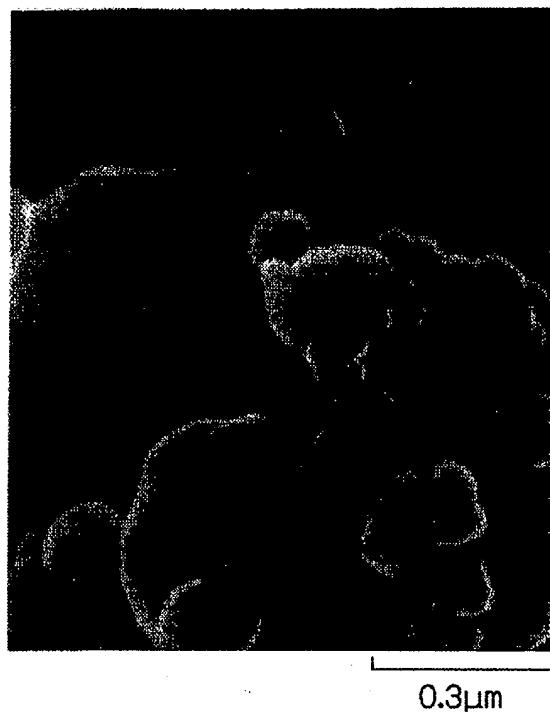
【図1】 実施例1の酸化銀-炭素複合材料のSEM写真である。

【図2】 比較例1の酸化銀のSEM写真である。

【図1】



【図2】



フロントページの続き

Fターム(参考) 5H003 AA02 AA04 BA01 BA02 BA05
BB00 BB04 BC05 BD01 BD02
5H015 AA02 AA07 BB02 BB05 BB10
DD01 DD07 EE06 EE13 HH00
HH01 HH13 HH17
5H016 AA02 BB02 BB05 BB11 CC00
CC09 EE01 EE05 HH01 HH11
HH13 HH17

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3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] A silver-oxide-graphite composite material characterized by coming to cover a silver-oxide (I) particle with a detailed carbon particle.

[Claim 2] A silver-oxide-graphite composite material characterized by coming to cover said silver-oxide (I) particle with this carbon particle while a carbon particle detailed in a (silver-oxide I) particle is included.

[Claim 3] Silver-oxide composite material given in either claim 1 to which the first [an average of] particle diameter of said silver-oxide (I) particle is 1.5 micrometers or less, and mean particle diameter of said carbon particle is characterized by 50A or more being 900A or less, or claim 2.

[Claim 4] A silver-oxide-graphite composite material according to claim 1 to 3 characterized by specific resistance when a consolidation is carried out by pressure of 2 t/cm² being 1000 or less ohm-cm.

[Claim 5] Positive active material for silver-oxide rechargeable batteries characterized by consisting of a silver-oxide-graphite composite material according to claim 1 to 4.

[Claim 6] A silver-oxide rechargeable battery characterized by coming to provide positive active material for silver-oxide rechargeable batteries according to claim 5.

[Claim 7] A manufacture method of a silver-oxide-graphite composite material characterized by making the surface of said silver-oxide (I) particle cover said carbon particle, adding a basic solution in a silver salt aqueous solution containing carbon particle powder with a mean particle diameter of 900A or less, and depositing a silver-oxide (I) particle.

[Claim 8] A manufacture method of a silver-oxide-graphite composite material characterized by making the surface of said silver-oxide (I) particle cover said carbon particle, adding a silver salt aqueous solution in a basic aqueous solution containing carbon particle powder with a mean particle diameter of 900A or less, and depositing a silver-oxide (I) particle.

[Claim 9] A manufacture method of a silver-oxide-graphite composite material according to claim 7 or 8 characterized by making said carbon particle include in a (silver-oxide I) particle in case a silver-oxide (I) particle is deposited.

[Claim 10] A manufacture method of a silver-oxide-graphite composite material according to claim 7 or 8 characterized by ranges of said A:B being 80:20-98:2 when a weight ratio of silver contained in said silver salt aqueous solution and said

[Claim 11] A manufacture method of a silver-oxide-graphite composite material according to claim 7 to 10 characterized by

[Claim 11] A manufacture method of a silver-oxide-graphite composite material according to claim 7 to 10 characterized by drying the aforementioned silver-oxide (I) particle by which the surface was covered with a carbon particle below 90 degrees C.

[Claim 12] A manufacture method of a silver-oxide-graphite composite material according to claim 7 to 10 characterized by carrying out the vacuum drying of the aforementioned silver-oxide (I) particle by which the surface was covered with a carbon particle.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the manufacture method of the positive active material for a silver-oxide-graphite composite material and silver-oxide rechargeable batteries, and a silver-oxide-graphite composite material.

[0002]

[Description of the Prior Art] There are a silver-oxide primary cell and a silver-oxide rechargeable battery in the cell which uses a silver oxide as positive active material. among these, a silver-oxide primary cell -- a positive electrode -- what mixed as a mixture the powder of the silver oxide (I) which is positive active material, and (Ag₂O), and the carbon particle powder or silver NIKKEI light powder which is an electric conduction assistant is used. although a silver oxide (I) and (Ag₂O) have low conductivity, it returns by advance of a discharge reaction -- having -- conductive metal silver (Ag) -- becoming -- a positive electrode -- the conductivity of a mixture improves with advance of discharge. Moreover, carbon particle powder and silver NIKKEI light powder act as electric conduction material in early stages of discharge. this -- the early stages of discharge -- setting -- a positive electrode -- since the content of the silver oxide (I) of a mixture and (Ag₂O) is high -- a positive electrode -- since the conductivity of a mixture becomes low -- the above-mentioned electric conduction assistant -- adding -- a positive electrode -- it is because it is necessary to raise the conductivity of a mixture.

[0003] on the other hand -- a silver-oxide rechargeable battery -- a silver-oxide primary cell -- the same -- a positive electrode -- at the time of discharge, a conductive low silver oxide (I) and (Ag₂O) are returned to a mixture even to conductive high metal silver (Ag) including the silver-oxide (I) (Ag₂O) powder which is positive active material, and the carbon particle powder which is an electric conduction assistant, and metal silver (Ag) oxidizes to a silver oxide (I) and (Ag₂O) at the time of charge. As for the reversible oxidation reduction reaction between this metal silver and a silver oxide (I), a reaction advances towards the interior of each particle from the surface of a metal silver granule child or a silver-oxide (I) particle. Therefore, when especially charge-and-discharge depth is deep, a conductive low silver oxide (I) forms in a metal silver granule child's surface thickly, and there is a possibility that electronic transfer may become difficult and it may become impossible to fully charge.

[0004] Then, by making small mean particle diameter of a silver-oxide (I) particle with 0.1-0.3 micrometers, effect of the conductive fall accompanying a deposit of a silver oxide (I) is made as small as possible, and invention about the silver-oxide rechargeable battery which was made to advance charge smoothly by this and has improved the charge-and-discharge property is indicated (JP,57-111955,A).

[0005]

[Problem(s) to be Solved by the Invention] however -- the conventional silver-oxide rechargeable battery -- a positive electrode -- a mixture -- the case where the carbon particle powder contained in inside **** -- it is -- a positive electrode -- a mixture -- there was a problem that the whole conductivity could not be raised.

[0006] Moreover, in aforementioned JP,57-111955,A, only an a maximum of 7 cycle degree can carry out the charge and discharge also of the charge and discharge test with a charge-and-discharge depth of 50%, but it has come to obtain a cell with it. [a short cycle life and] [practical] since the silver oxide (I) this [whose] is an insulating material in the charge last stage deposits -- a positive electrode -- it was for the conductivity of a mixture to fall.

[0007] this invention is made in view of the above-mentioned situation -- having -- a positive electrode -- the conductivity of a mixture is raised, and charge-and-discharge effectiveness of a silver-oxide rechargeable battery is made high, and it aims at offering the silver-oxide-graphite composite material which can be lengthened and its manufacture method of a cycle life.

[0008]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention adopted the following configurations. A silver-oxide-graphite composite material of this invention is characterized by coming to cover a silver-oxide (I) particle with a detailed carbon particle. Moreover, a silver-oxide-graphite composite material of this invention is characterized by coming to cover said silver-oxide (I) particle with this carbon particle while a carbon particle detailed in a (silver-oxide I) particle is included.

[0009] As for the first [an average of] particle diameter of said silver-oxide (I) particle, it is desirable that it is 1.5 micrometers or less, and, as for mean particle diameter of said carbon particle, it is desirable that it is [50A or more] 900A or less. Moreover, as for the first [an average of] particle diameter of said silver-oxide (I) particle, it is more desirable that it is

0.1 micrometer or more] 1.5 micrometers or less, and it is still more desirable that it is [0.2 micrometer or more] 1.0 micrometers or less. Moreover, as for mean particle diameter of said carbon particle, it is more desirable that it is [100A or more] 500A or less.

[0010] This silver-oxide-graphite composite material on the surface of a silver-oxide (I) particle [whether covering formation of the carbon particle is carried out uniformly, and] Or while a carbon particle is included inside a silver-oxide (I) particle, it comes to carry out covering formation of the carbon particle on the surface of a silver-oxide (I) particle. Since a conductive network will be formed of a carbon particle if consolidation of the powder of this silver-oxide-graphite composite material is carried out When this silver-oxide-graphite composite material is used as positive active material for silver-oxide rechargeable batteries, even if a silver oxide generates with advance of charge, specific resistance of positive active material does not become high, and charge-and-discharge effectiveness of a silver-oxide rechargeable battery can be made high. Moreover, if the first [an average of] particle diameter of a silver-oxide (I) particle is the above-mentioned range, a charge-and-discharge reaction can be advanced efficiently and charge-and-discharge effectiveness of a silver-oxide rechargeable battery can be made high.

[0011] Moreover, a silver-oxide-graphite composite material of this invention has that desirable whose specific resistance when carrying out a consolidation by pressure of 2 t/cm² is 1000 or less ohm-cm, and what is 300 or less ohm-cm is more desirable.

[0012] a positive electrode of a silver-oxide rechargeable battery [in / since specific resistance at the time of consolidation was 1000 or less ohm-cm, when this silver-oxide-graphite composite material is used as positive active material for silver-oxide rechargeable batteries according to this silver-oxide-graphite composite material / the charge last stage] -- specific resistance of a mixture can be made low and charging efficiency can be made high.

[0013] Positive active material for silver-oxide rechargeable batteries of this invention consists of the above-mentioned silver-oxide-graphite composite material. And a silver-oxide rechargeable battery of this invention comes to provide positive active material for the above-mentioned silver-oxide rechargeable batteries. since this silver-oxide rechargeable battery possesses the above-mentioned positive active material -- a positive electrode -- while being able to make conductivity of a mixture high and being able to make charge-and-discharge effectiveness high, a cycle life can be developed sharply.

[0014] It is characterized by making the surface of said silver-oxide (I) particle cover said carbon particle, a manufacture method of a silver-oxide-graphite composite material of this invention adding a basic solution in a silver salt aqueous solution containing carbon particle powder with a mean particle diameter of 900A or less, and depositing a silver-oxide (I) particle. Moreover, the surface of said silver-oxide (I) particle may be made to cover said carbon particle, adding a silver salt solution in a basic aqueous solution containing carbon particle powder with a mean particle diameter of 900A or less, and depositing a silver-oxide (I) particle. If said carbon particle has suspended in a silver salt aqueous solution, in case a silver-oxide (I) particle is deposited, it will become that it is easy to make said carbon particle include in a (silver-oxide I) particle.

[0015] As the above-mentioned carbon particle, 900A or less of 50A or more 900A or less of mean particle diameter, such as a carbon black particle, a mesophase pitch particle, a pitch particle, and a graphite particle, of 100A or more thing 500A or less is more preferably good preferably. Moreover, aqueous solutions, such as a silver nitrate, can be illustrated as the above-mentioned silver salt aqueous solution. Furthermore, as the above-mentioned basic solution, basic aqueous solutions, such as a potassium hydroxide and a sodium hydroxide, can be illustrated.

[0016] For example, if basic solutions, such as a potassium-hydroxide aqueous solution, are added in silver salt aqueous solutions, such as a silver-nitrate aqueous solution, a silver oxide (I) and (Ag₂O) deposit. If a carbon particle detailed in a silver salt solution is added in the state of suspension, grain growth of a silver-oxide (I) (Ag₂O) particle will be checked by carbon particle, and mean particle diameter of a silver-oxide (I) particle will become small. Furthermore, a suspended carbon particle carries out deposition to the surface of a silver-oxide (I) particle, and a silver-oxide (I) particle is covered with a carbon particle. Moreover, in case a silver-oxide (I) particle deposits, a carbon particle may be incorporated in a (silver-oxide I) particle. Therefore, according to a manufacture method of a silver oxide for these silver-oxide rechargeable batteries, mean particle diameter is small and a silver-oxide (I) particle by which the whole surface was covered with a carbon particle can be obtained easily.

[0017] Moreover, when a weight ratio of silver contained in said silver salt aqueous solution and said carbon particle powder is made into A:B (A is the weight of silver in a silver salt solution, and B is the weight of carbon particle powder), it is desirable that ranges of said A:B are 80:20-98:2. Moreover, as for above-mentioned A:B, it is more desirable that it is 88:12-96:4. If a weight ratio of carbon particle powder and silver is in above-mentioned within the limits, the (silver-oxide I) particle surface can be made to cover a carbon particle uniformly.

[0018] Furthermore, it is desirable to dry preferably the 90 degrees C or less of the aforementioned silver-oxide (I) particles by which the surface was covered with a carbon particle below 70 degrees C. As for a desiccation ambient atmosphere at this time, it is desirable to carry out in atmospheric air or an inert gas ambient atmosphere. Moreover, the vacuum drying of the aforementioned silver-oxide (I) particle by which the surface was covered with a carbon particle may be carried out. As for drying temperature at the time of carrying out a vacuum drying, it is desirable to consider as 70 degrees C or less, and it may carry out freeze-dry lyophilization.

[0019] If it dries within the limits of the above-mentioned conditions, a carbon particle and a silver-oxide (I) particle will not carry out the combustion reaction of the aforementioned silver-oxide (I) particle by which the surface was covered with a carbon particle during desiccation.

[0020]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained with reference to a drawing. It comes to cover this invention silver-oxide-graphite composite material with a carbon particle with a detailed silver-oxide (I) (Ag_2O) particle. Moreover, while a carbon particle with the silver-oxide-graphite composite material of this invention detailed in a (silver-oxide I) particle is included, you may come to cover said silver-oxide (I) particle with a carbon particle. [0021] As for the silver-oxide-graphite composite material of this invention, it is desirable for it to be used as positive active material of a silver-oxide primary cell or a silver-oxide rechargeable battery, and to be used especially for a silver-oxide rechargeable battery. When this silver-oxide-graphite composite material is used for a silver-oxide primary cell, a silver oxide (I) and (Ag_2O) are returned even to conductive metal silver (Ag) in the case of discharge. Moreover, when a silver-oxide-graphite composite material is used for a silver-oxide rechargeable battery, a silver oxide (I) and (Ag_2O) are returned even to conductive metal silver (Ag) at the time of discharge, and metal silver (Ag) oxidizes to a silver oxide (I) and (Ag_2O) at the time of charge. As for the reversible oxidation reduction reaction between the metal silver in a silver-oxide rechargeable battery, and a silver oxide (I), a reaction advances towards the interior of each particle from the surface of a metal silver granule child or a silver-oxide (I) particle. Therefore, when especially charge-and-discharge depth is deep, the silver oxide (I) which is an insulating material forms in a metal silver granule child's surface thickly, and there is a possibility that electronic transfer may become difficult and it may become impossible to fully charge.

[0022] So, the silver-oxide-graphite composite material which comes to carry out covering formation of the carbon particle uniformly consisted of this inventions on the surface of a silver-oxide (I) particle. the powder of this silver-oxide-graphite composite material carries out consolidation -- having -- the positive electrode of a silver-oxide rechargeable battery -- if a mixture is formed, a conductive network will be formed of a carbon particle. Therefore, even if the silver oxide which is an insulating material generates with advance of charge, the specific resistance of the silver-oxide-graphite composite material itself does not become high by the conductive network of a carbon particle, and charge-and-discharge effectiveness can be made high. Moreover, if a carbon particle is included in a (silver-oxide I) particle, the conductivity of the (silver-oxide I) particle itself can be raised, the specific resistance of the silver-oxide-graphite composite material itself will not become high, and charge-and-discharge effectiveness of a silver-oxide rechargeable battery can be made high.

[0023] Moreover, as for a carbon particle, it is desirable to cover the surface of a silver-oxide (I) particle to homogeneity uniformly. If a carbon particle does not cover a silver-oxide (I) particle uniformly, since a carbon particle will segregate, it will become impossible to form a uniform conductive network and charge-and-discharge effectiveness will fall, it is not desirable.

[0024] 0.1 micrometers or more 1.5 micrometers or less of 1.5 micrometers or less of first [an average of] particle diameter of a silver-oxide (I) particle of the silver-oxide-graphite composite material of this invention are more preferably good in it being 0.2-micrometer or more thing 1.0 micrometers or less still more preferably. If the first [an average of] particle size of a silver-oxide (I) particle exceeds 1.5 micrometers, since a silver oxide (I) will cover metal silver thickly at the time of charge, it will become impossible to oxidize metal silver more than it, a charge reaction will be checked and charge-and-discharge effectiveness will fall, it is not desirable. Moreover, since even the metal silver a part of whose silver oxide (I) is a discharge product about a silver-oxide (I) particle as the first [an average of] particle size is less than 0.1 micrometers will be returned by the wrap carbon particle and the rate of self-discharge of a silver-oxide rechargeable battery becomes high, it is not desirable. If the first [an average of] particle diameter of a silver-oxide (I) particle is within the limits of the above, a charge-and-discharge reaction can be advanced efficiently and charge-and-discharge effectiveness can be made high.

[0025] Moreover, as for the mean particle diameter of a wrap carbon particle, it is desirable that it is 50A or more 900A or less about a silver-oxide (I) particle, and it is more desirable that it is [100A or more] 500A or less. Since the activity of a carbon particle becomes it very high that the mean particle diameter of a carbon particle is less than 50A, there is a possibility of returning a silver oxide (I) to metal silver and the rate of self-discharge of a silver-oxide rechargeable battery becomes high, it is not desirable. Moreover, since it becomes impossible for a carbon particle to cover a silver-oxide (I) particle uniformly and it becomes impossible to form a conductive network when the mean particle diameter of a carbon particle exceeds 900A, it is not desirable.

[0026] Moreover, as for the silver-oxide-graphite composite material of this invention, it is desirable that the specific resistance when carrying out a consolidation by the pressure of 2 t/cm² is 1000 or less ohm-cm, and it is more desirable that they are 300 or less ohm-cm. if specific resistance exceeds 1000 ohm-cm -- the positive electrode of a silver-oxide rechargeable battery -- since the conductivity of a mixture will fall and charge-and-discharge effectiveness falls, it is not desirable. Specific resistance is greatly influenced by the covering condition of a wrap carbon particle in a silver-oxide (I) particle. That is, specific resistance will become high if a carbon particle is unevenly distributed on the surface of a silver-oxide (I) particle. As for a carbon particle, it is desirable also from this to cover a silver-oxide (I) particle to homogeneity uniformly.

[0027] The above-mentioned silver-oxide-graphite composite material can be suitably used as positive active material of a silver-oxide rechargeable battery. As a silver-oxide rechargeable battery, the so-called carbon button type of silver-oxide rechargeable battery can be illustrated here. that the silver-oxide-graphite composite material powder of this invention of this silver-oxide rechargeable battery is independent, or the positive electrode which fabricated to the pellet type what added electric conduction assistants, such as a graphite, to silver-oxide-graphite composite material powder -- it is constituted by a mixture, negative-electrode gel zinc, a separator, the electrolytic solution, and the cell container that contains these.

[0028] Negative-electrode gel zinc comes to mix the **-ized zinc powder which added and amalgamated mercury for example, into zinc powder, gelling agents, such as a carboxymethyl cellulose, and the electrolytic solution. Moreover, what

dissolved the zinc oxide in the aqueous solutions or these mixed solutions of the either a sodium hydroxide or the potassium hydroxides can be used for the electrolytic solution. Furthermore, a separator is constituted considering cellophane as a subject, in order to prevent diffusion of complex ion, carries out the laminating of the polyethylene graft--ization-processed, for example to cellophane, and is constituted.

[0029] Next, the manufacture method of the silver-oxide-graphite composite material of this invention is explained. The manufacture method of the silver-oxide-graphite composite material of this invention is a thing of making the surface of said silver-oxide (I) particle cover said carbon particle, depositing a silver-oxide (I) particle by adding a basic solution in the silver salt aqueous solution containing carbon particle powder with a mean particle diameter of 900A or less. As for a carbon particle, having suspended in a silver salt aqueous solution is desirable. Moreover, a silver salt nature solution may be added in the basic aqueous solution containing carbon particle powder with a mean particle diameter of 900A or less. Moreover, in case a silver-oxide (I) particle is deposited, said carbon particle may be made to include in a (silver-oxide I) particle.

[0030] For example, if basic solutions, such as a potassium-hydroxide aqueous solution, are added in silver salt aqueous solutions, such as a silver-nitrate aqueous solution, a silver oxide (I) and (Ag₂O) deposit. Here, if the carbon particle detailed in a silver salt solution is added in the state of suspension, grain growth of a silver-oxide (I) (Ag₂O) particle will be checked by the carbon particle, and the mean particle diameter of a silver-oxide (I) particle will become small. Furthermore, the suspended carbon particle carries out deposition to the surface of a silver-oxide (I) particle, and a silver-oxide (I) particle is covered with a carbon particle. Moreover, in case a silver-oxide (I) particle deposits, a carbon particle may be incorporated in a (silver-oxide I) particle. Therefore, according to the manufacture method of this silver-oxide-graphite composite material, mean particle diameter is small and the silver-oxide (I) particle by which the whole surface was covered with the carbon particle can be obtained easily.

[0031] As the above-mentioned carbon particle, 900A or less of 50A or more 900A or less of mean particle diameter, such as a carbon black particle, a mesophase pitch particle, a pitch particle, and a graphite particle, of 100A or more thing 500A or less is more preferably good preferably. Since there is a possibility of the activity of a carbon particle becoming very high, and there being a possibility that a carbon particle may light, at the time of desiccation of the silver oxide (I) mentioned later, and returning a silver oxide (I) to metal silver when the mean particle diameter of a carbon particle is less than 50A, it is not desirable. Moreover, since there is a possibility that it may become impossible to check grain growth of a silver oxide (I) effectively, and a silver-oxide (I) particle may ***** and there is a possibility that it may become impossible to cover a silver-oxide (I) particle with a carbon particle uniformly, and it may become impossible to form a conductive network in case a silver oxide (I) is made to generate when the mean particle diameter of a carbon particle exceeds 900A, it is not desirable.

[0032] Moreover, as the above-mentioned silver salt aqueous solution, silver salt aqueous solutions, such as a silver nitrate, can be illustrated. Furthermore, as the above-mentioned basic solution, basic aqueous solutions, such as a potassium hydroxide and a sodium hydroxide, can be illustrated.

[0033] Moreover, when the weight ratio of the silver contained in a silver salt aqueous solution and said carbon particle powder is made into A:B (A is the weight of the silver in a silver salt solution, and B is the weight of carbon particle powder), it is desirable that the ranges of said A:B are 80:20-98:2, and it is more desirable that it is 88:12-96:4. a weight ratio -- if a silver weight ratio (A) becomes small rather than the case of A:B=80:20, since the moldability of the silver-oxide-graphite composite material obtained will fall -- the powder of a silver-oxide-graphite composite material -- a consolidation -- carrying out -- a positive electrode -- the time of fabricating a mixture -- a positive electrode -- a mixture -- a crack -- easy -- since it becomes, it is not desirable. Moreover, since it becomes impossible for the amount of carbon particles to be able to be insufficient, and for a carbon particle to be unevenly distributed to a silver-oxide (I) particle, and to make the (silver-oxide I) particle surface cover a carbon particle to homogeneity uniformly when a silver weight ratio (A) becomes large rather than the case of A:B=98:2, it is not desirable. If the weight ratio of carbon particle powder and silver is in above-mentioned within the limits, the silver-oxide-graphite composite material which could make the (silver-oxide I) particle surface cover a carbon particle uniformly, and was excellent in the moldability will be obtained.

[0034] It is desirable that the 40 or more g/L range of the concentration of the silver contained in a silver salt aqueous solution is 700 or less g/L, and, specifically, it is more desirable that it is the 200 or more g/L range of 500 or less g/L. Moreover, it is desirable that the 3 or more g/L range of the concentration of the carbon particle powder contained in a silver salt aqueous solution or a basic aqueous solution is 60 or less g/L, and it is more desirable that it is the 10 or more g/L range of 30 or less g/L.

[0035] As for the silver-oxide (I) particle covered with the carbon particle, drying below 70 degrees C is preferably desirable 90 degrees C or less. As for the desiccation ambient atmosphere at this time, it is desirable to carry out in atmospheric air or an inert gas ambient atmosphere. Since there is a possibility of there being a possibility that a carbon particle may light and returning a silver oxide (I) to metal silver when drying temperature exceeds 90 degrees C, it is not desirable.

[0036] Moreover, it is more desirable to replace with the above-mentioned stoving and to carry out the vacuum drying of the silver-oxide (I) particle covered with the carbon particle. As for the drying temperature at the time of carrying out a vacuum drying, it is desirable to consider as that [70 degrees C or less], and it may carry out freeze drying. In order to react if a carbon particle is heated, to tend to return a silver oxide (I) and to prevent this reaction, it is still more effective the vacuum drying in a room temperature or a low-temperature vacuum drying 10 degrees C or less, and to perform freeze-dry lyophilization -5 degrees C or less.

[0037] A silver-oxide-graphite composite material can be dried without a carbon particle and a silver-oxide (I) particle reacting, if the silver-oxide (I) particle covered with the carbon particle is dried within the limits of the above-mentioned

conditions.

[0038] Since a conductive network will be formed of a carbon particle if it comes to carry out covering formation of the carbon particle uniformly and consolidation of this powder is carried out to the surface of a silver-oxide (I) particle, even if a silver oxide generates the above-mentioned silver-oxide-graphite composite material with advance of charge, the specific resistance of a silver-oxide-graphite composite material does not become high, and it can make charge-and-discharge effectiveness high.

[0039] Moreover, since the carbon particle which grain growth of a silver-oxide (I) (Ag_2O) particle was checked by the carbon particle, and has suspended further carries out deposition to the surface of a silver-oxide (I) particle according to the manufacture method of the above-mentioned silver-oxide-graphite composite material, mean particle diameter is small and the silver-oxide-graphite composite material with which the whole surface consists of a silver-oxide (I) particle covered with the carbon particle can be obtained easily.

[0040]

[Example] (Manufacture of the silver-oxide-graphite composite material of examples 1-5) Silver concentration supplied carbon black with a mean particle diameter of 50-900A to the silver-nitrate aqueous solution which is 400 g/L, and considered as the suspension condition. Stirring this silver nitrate solution, the sodium-hydroxide aqueous solution of 5 conventions was added until the silver-nitrate aqueous solution was set to pH13, and the silver oxide (I) was deposited. In addition, when adding a sodium-hydroxide aqueous solution in a silver-nitrate aqueous solution, the temperature control was performed so that solution temperature might maintain 25 degrees C. Next, after repeating a decantation and stirring washing by distilled water by a unit of 7 times to this silver oxide (I), stoving or a vacuum drying was performed. thus, the silver-oxide-graphite composite material of examples 1-5 -- having manufactured. Correspondence of the mean particle diameter of each silver-oxide-graphite composite material and carbon black is shown in a table 1. Moreover, the weight ratio of the silver in a silver-nitrate aqueous solution and carbon black is collectively shown in a table 1. Furthermore, desiccation conditions are collectively shown in a table 1.

[0041] (Manufacture of the silver-oxide-graphite composite material of the examples 1-4 of a comparison) Silver concentration stirring the silver-nitrate aqueous solution of 40 g/L, the sodium-hydroxide aqueous solution of 0.5 conventions was added until the silver-nitrate aqueous solution was set to pH12, and the silver oxide (I) was deposited. In addition, when adding a sodium-hydroxide aqueous solution in a silver-nitrate aqueous solution, the temperature control was performed so that solution temperature might maintain 8 degrees C. Next, carbon black was blended dryly, after repeating a decantation and stirring washing by distilled water 7 times to this silver oxide (I) and carrying out stoving at 160 degrees C. Thus, the silver oxide of the example 1 of a comparison was manufactured. Manufacture conditions are shown in a table 1. Furthermore, the silver-oxide-graphite composite material of the examples 2-4 of a comparison was manufactured like examples 1-5 except having changed the weight ratio of silver and carbon black, and the mean particle diameter of carbon black. Manufacture conditions are shown in a table 1.

[0042] The silver oxide of examples 1-5 and the example 1 of a comparison was observed with the scanning electron microscope (SEM). The SEM photograph of the example 1 photoed at this time and the example 1 of a comparison is shown in drawing 1 and drawing 2. It turns out that the surface of the silver-oxide-graphite composite material of an example 1 is uniformly covered with the detailed carbon black particle with a particle size of about 200A so that clearly from drawing 1. Moreover, it is presumed that the bottom of a carbon black particle is a silver oxide (I), and it turns out that the primary [an average of] particle diameter is about 1 micrometer. Moreover, the primary [an average of] particle diameter of the silver oxide (I) which constitutes the silver-oxide-graphite composite material of examples 2-5 is as being shown in a table 2, and it turns out that all are 1.5 micrometers or less. On the other hand, in the surface of the silver oxide of the example 1 of a comparison, a grain-like particle was not seen at all, and the primary [an average of] particle diameter of this silver oxide was 0.3 micrometers from a table 2.

[0043] Next, the consolidation object of the shape of a rectangular parallelepiped of 3mmx2.7mmx30mm magnitude was acquired by putting 1g of powder of the silver-oxide-graphite composite material of examples 1-5 and the examples 1-4 of a comparison into shaping metal mold, respectively, and carrying out a consolidation by the pressure of 2 t/cm². In addition, in the example 1 of a comparison, the consolidation of the carbon black of 5 % of the weight of 500A mean particle diameter was added and carried out to the silver oxide of the example 1 of a comparison. And specific resistance was measured for the electrode for specific resistance measurement by installation and 4 terminal method on each consolidation object. A result is shown in a table 2. Specific resistance is 1000 or less ohm-cm, and it turns out that each silver-oxide-graphite composite material of examples 1-5 is smaller than the specific resistance of the silver oxide of the examples 1-3 of a comparison so that clearly from a table 2.

[0044] the carbon black which it added that it was not involved that carbon black is added by the silver oxide of the example 1 of a comparison, either, but specific resistance became higher than the silver-oxide-graphite composite material of examples 1-5 distributes to homogeneity -- not having -- consolidation -- since it was unevenly distributed in the inside of the body, it is presumed because a-uniform conductive network was not formed. Moreover, it is silver:CB=99:1, since the weight ratio of carbon black was small, as for the silver oxide of the example 2 of a comparison, the weight ratio of the silver at the time of manufacture and carbon black (CB) cannot cover the surface of a silver-oxide particle with carbon black uniformly, but specific resistance is considered to have become high. Furthermore, since the silver oxide of the example 3 of a comparison has the mean particle diameter of carbon black as excessive as 1500A, it cannot cover the surface of a silver-oxide particle with carbon black uniformly, but is considered that specific resistance became high.

[0045] next, the powder of the silver-oxide-graphite composite material of examples 1-5 and the examples 1-4 of a comparison -- a consolidation -- carrying out -- a disc-like positive electrode with a diameter [of 11mm], and a thickness of 2mm -- it considered as the mixture. In addition, in the example 1 of a comparison, the carbon black of 5 % of the weight of 500A mean particle diameter other than a silver oxide was added. Moreover, the carboxymethyl cellulose and the sodium-hydroxide aqueous solution were added into the **-ized zinc powder which contains lead 0.5% of the weight, and it considered as negative-electrode gel zinc. these positive electrodes -- while containing a mixture and negative-electrode gel zinc in a cell container -- a positive electrode -- the silver-oxide rechargeable battery of a carbon button mold with a diameter [of 11.6mm] and a height of 4.2mm was manufactured by isolating a mixture and negative-electrode gel zinc with the separator made from cellophane, and adding the electrolytic solution which contains a little zinc oxide in 30 more% of the weight of a sodium hydroxide.

[0046] Charge and discharge were performed for the obtained cell for 3mA of charging currents, and charging-time 40 hours on condition that 3mA of discharge currents, and discharge-final-voltage 1.0V. 5 when making first time discharge capacity into 100% and the 10 or 20th discharge capacity factor are shown in a table 2. The 10th discharge capacity of the silver-oxide rechargeable battery of the example 1 of a comparison has turned into about 29% of the discharge capacity which is the 1st time to the 20th discharge capacity of the silver-oxide rechargeable battery of examples 1-5 being 70% or more of the discharge capacity which is the 1st time so that clearly from a table 2. Therefore, according to the silver-oxide-graphite composite material of examples 1-5, charge-and-discharge effectiveness is higher than the silver oxide of the example 1 of a comparison, and it turns out that a cycle life can constitute a long silver-oxide rechargeable battery. Moreover, since it is high, as for the silver oxide cell of the example 2 of a comparison, and the example 3 of a comparison, no specific resistance of a silver-oxide-graphite composite material can perform charge and discharge smoothly, but it is thought that discharge capacity fell. Furthermore, with the silver oxide cell of the example 4 of a comparison, since the drying temperature at the time of manufacturing a silver-oxide-graphite composite material was as high as 90 degrees C, a part of silver oxide is returned, silver deposits, and it is thought that discharge capacity fell by this.

[0047]

[A table 1]

	銀とカーボンブラック粒子 (C B)の重量比	カーボンブラック粒子 の平均粒径(Å)	乾燥条件
実施例 1	銀 : C B = 9 0 : 1 0	2 0 0	真空、1 0 ℃
実施例 2	銀 : C B = 8 8 : 1 2	4 0 0	真空、- 7 ℃(冷凍)
実施例 3	銀 : C B = 9 6 : 4	1 0 0	大気、6 0 ℃
実施例 4	銀 : C B = 9 7 : 3	6 0	大気、2 5 ℃
実施例 5	銀 : C B = 8 2 : 1 8	8 0 0	真空、6 0 ℃
比較例 1	銀 : C B = 9 6 : 4	4 0 0	-
比較例 2	銀 : C B = 9 9 : 1	1 0 0	真空、6 0 ℃
比較例 3	銀 : C B = 9 0 : 1 0	1 5 0 0	真空、6 0 ℃
比較例 4	銀 : C B = 9 0 : 1 0	1 0 0	真空、9 0 ℃

[0048]

[A table 2]

	カーボンブラック 粒子の平均粒径(Å)	酸化銀(I)の平均 1次粒子径(μm)	圧密体の比抵抗 (Ω・cm)	5回目放電 容量比(%)	10回目放電 容量比(%)	20回目放電 容量比(%)
実施例1	200	0.5	120	81	79	75
実施例2	400	1.0	230	79	75	74
実施例3	100	0.4	170	80	78	74
実施例4	60	0.2	610	78	74	71
実施例5	800	1.4	850	77	73	70
比較例1	400	0.3	11500	38	29	15
比較例2	100	0.9	5700	51	48	44
比較例3	1500	1.6	6500	57	51	46
比較例4	100	0.4	15	65	60	49

[0049]

[Effect of the Invention] As mentioned above, as explained to details, since a conductive network will be formed of a carbon particle if covering formation is carried out, a carbon particle becomes the surface of a silver-oxide (I) particle uniformly and consolidation of the powder of this silver-oxide-graphite composite material is carried out, even if a silver oxide generates the silver-oxide-graphite composite material of this invention with advance of charge, the specific resistance of a silver-oxide-graphite composite material does not become high, and it can make high charge-and-discharge effectiveness of a silver-oxide rechargeable battery. Moreover, since the first [an average of] particle diameter of a silver-oxide (I) particle is 1.5 micrometers or less, a charge-and-discharge reaction can be advanced efficiently and charge-and-discharge effectiveness of a silver-oxide rechargeable battery can be made high. Moreover, since the mean particle diameter of a wrap carbon particle is 900A or less about a silver-oxide (I) particle, a silver-oxide (I) particle can be uniformly covered with a carbon particle.

[0050] moreover, the positive electrode of the silver-oxide rechargeable battery in the charge last stage since the specific resistance at the time of consolidation is 1000 or less ohm-cm according to the silver-oxide-graphite composite material of this invention -- specific resistance of a mixture can be made low and charging efficiency of a silver-oxide rechargeable battery can be made high. in addition -- since the silver-oxide-graphite composite material of this invention is once granulated -- a positive electrode -- a mixture can also be manufactured.

[0051] Moreover, since a carbon particle comes uniformly to provide the positive active material which comes to carry out covering formation on the surface of a silver-oxide (I) particle, the silver-oxide rechargeable battery of this invention can develop a cycle life sharply while being able to make charge-and-discharge effectiveness high.

[0052] The manufacture method of the silver-oxide-graphite composite material of this invention Since the surface of this particle is made to cover with said carbon particle while forming a silver-oxide (I) particle by adding a basic solution into the silver salt aqueous solution containing carbon particle powder with a mean particle diameter of 900A or less Grain growth of a silver-oxide (I) (Ag₂O) particle is checked by the carbon particle, the carbon particle suspended further carries out deposition to the surface of a silver-oxide (I) particle, mean particle diameter is small and the silver-oxide (I) particle by which the whole surface was covered with the carbon particle can be obtained easily.

[0053] Moreover, since the ranges of said A:B are 80:20-98:2 when the weight ratio of the silver contained in said silver salt aqueous solution and said carbon particle powder is made into A:B (A is the weight of the silver in a silver salt solution, and B is the weight of carbon particle powder), the (silver-oxide I) particle surface can be made to cover a carbon particle uniformly.

[0054] Furthermore, if a vacuum drying is carried out, ignition of a carbon particle or the reduction of ** which dries the silver-oxide (I) particle covered with the carbon particle below 90 degrees C, or a silver oxide (I) by the carbon particle can be prevented.

[Translation done.]